

INVESTIGATING CATALYST-SUPPORT INTERACTIONS IN A PT(II/IV) CYCLE FOR SELECTIVE ALKANE OXIDATION

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INTRODUCTION

The selective oxidation and functionalization of alkanes is an important problem in this age of increased energy efficiency and conservation. Methane functionalization in particular, is of great importance for the generation of transportable chemical feedstocks. The major problem in most systems is over-oxidation, as the initial CH bond in methane is stronger than those of the corresponding oxidation products.¹ Additionally, classic radical functionalization routes yield less desirable branched products in larger alkanes. Organometallic systems are known to have the desired selectivity for primary over secondary and tertiary CH bonds and over-oxidation can be mitigated through the choice of supporting ligands.¹ This project studies the metal ligation and catalyst-support interactions in a series of single-site, surface-supported organometallic systems to aid in the development of novel alkane oxidation catalysts.



Well defined supported single-site alkane oxidation catalysts are not known, however, the solution chemistry of group 10 transition metals for the conversion of alkanes to alcohols and alkyl chlorides is particularly rich. In 1983, Shilov and co-workers demonstrated that aqueous $[\text{Pt}^{\text{II}}\text{Cl}_4]^{2-}$ catalytically oxidizes methane to methanol and methylchloride.² The system requires $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ as a stoichiometric oxidant, problematic for large scale applications. More recently, Catalytica developed a system using (2,2'-bipyrimidine) $\text{Pt}^{\text{II}}\text{Cl}_2$ in hot H_2SO_4 .³ In both systems the active catalyst is a coordinatively unsaturated platinum(II) species. The mechanism involves electrophilic CH bond activation to form a square planar (alkyl) Pt^{II} species. After oxidation, product is released by nucleophilic attack. The mechanism is general for ligands of greatly varied steric and electronic bulk.¹

We will synthesize a series of molecular platinum(II) species as site-isolated catalysts on solid supports in order to study the selective oxidation reactions of alkanes. This will favor the coordinatively unsaturated intermediates proposed for both the Shilov and Catalytica cycles, and disfavor the dominant solution deactivation routes. Based on the known homogenous literature, an idealized catalytic cycle for the supported material is shown in Figure 1. As this project is still in its infancy, only preliminary results will be described. Longer term goals include varying the ligand environment on our supported catalysts to focus on maintaining or improving the unique selectivity patterns reported in the solution literature.

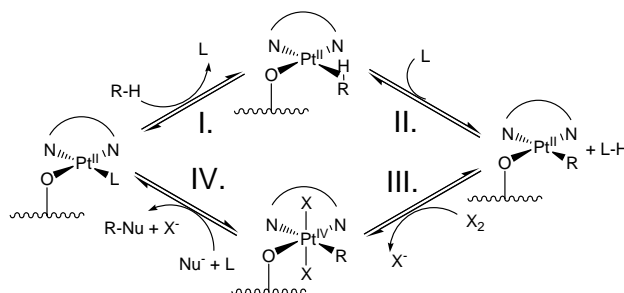


Figure 1: Proposed catalytic oxidation cycle based on the homogenous catalysis literature. Initial coordination (I) and deprotonation (II) of the alkane is followed by oxidation by (III) and nucleophilic attack (IV) to release product.

RESULTS

Platinum precursors: We have chosen to synthesize a series of platinum allyl complexes including; $\text{Pt}(\text{C}_4\text{H}_6)_2$, $[\text{Pt}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_4$, $[\text{Pt}(\eta^3\text{-C}_4\text{H}_6)\text{Cl}]_2$. Grafting reactions with hydroxylated supports are known in the literature, although the grafting stoichiometry and reactivity with alkanes have not been studied in detail.⁴ Recent progress in the synthesis of the molecular precursors will be described.

Catalyst supports: A series of partially and fully dehydroxylated $\gamma\text{-Al}_2\text{O}_3$ supports have been prepared by heating under flowing helium. Different dehydroxylation temperatures yield surface areas ranging between 100 and 300 m^2g^{-1} . These variations in surface area indicate a difference in surface hydroxyl content and accessibility. The number of accessible hydroxyl groups may affect the grafting reaction with our platinum allyl precursors.

Catalytic System: Design of a flow-through reactor system for catalyst testing as well as preliminary grafting experiments will also be discussed.

REFERENCES

- (a) R.H. Crabtree. *J. Organomet. Chem.* 689, 4083-4091 (2004). (b) U. Fekl, K.I. Goldberg. *Adv. Inorg. Chem.*, 54, 259-320 (2003). (c) Activation and Functionalization of C-H Bonds, K.I. Goldberg and A.S. Goldman, Editors, p.250-356, ACS Symposium Series 885; American Chemical Society, Washington, DC (2004).
- (a) Y.V. Geletii, A.E. Shilov, *Kin. Catal.*, 24, 413-416, (1983). (b) S.S. Stahl, J.A. Labinger, J.E. Bercaw, *Angew. Chem. Int. Ed.*, 37, 2181 (1998).
- R.A. Periana, D.J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science*, 280, 560-563 (1998).
- (a) J.M. Chance, D.L. Linebarrier, T.A. Nile, *Transition Met. Chem.*, 12, 276-277 (1987). (b) S.K. Purnell, K.M. Sanchez, R. Patrini, J.-R. Chang, B.C. Gates, *J. Phys. Chem.*, 98, 1205-1212 (1994).

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